



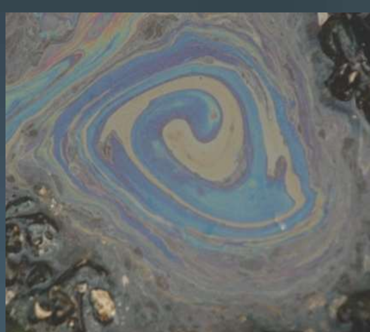


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Harnessing science and technology to assist clients with their challenging problems and issues.

Evaluation of Different Source Preparation and Selection Strategies in Chemical Mass Balance Modeling: Multiple Polycyclic Aromatic Hydrocarbon Sources to Urban Lake Sediments

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August 9, 2015

National Environmental Monitoring Conference

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Presentation Outline

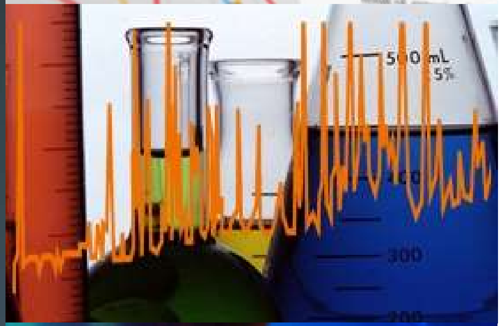
- Introduction
  - Environmental Forensics
  - Chemical Mass Balance (CMB) model as a tool
    - What is it?
    - How does it work?
    - What would you get?
- Case Study I & II
- Conclusion

Apportionment of Liability and Allocation of Costs

- A frequent issue in CERCLA and other cases involving contribution claims is the *apportionment of liability and allocation of the response costs* among two or more responsible parties
- While the legal basis and evidentiary requirements differ for apportionment and allocation, both are bolstered by *technically defensible estimates of each party's contribution of contaminants*

Our Technical Toolbox

- Industrial archeology
  - Public and private records
- Process understanding
  - Refineries, MGPs, chemical plants, mining
- Environmental Forensics
  - Chemical fingerprinting
  - Data analytics
- Fate and transport modeling
  - Ground and surface water
  - Air and depositional modeling
  - Biotransformation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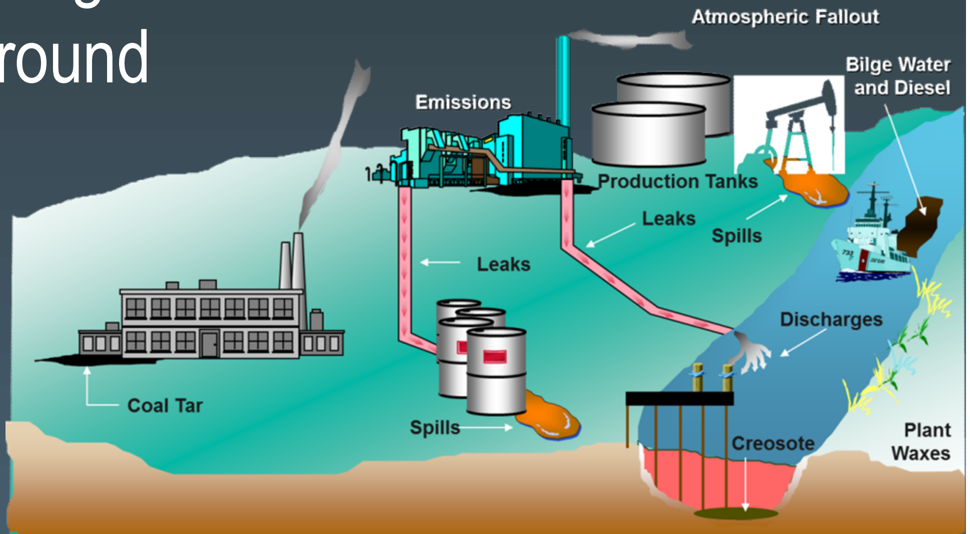
Environmental Forensics Can be Used in a Systematic Fashion in Support of Apportionment and Allocation

- Identification of potential sources
- Chemical characterization of the potential sources (i.e. PRP “fingerprints”), including anthropogenic background, that are affecting a site
- Evaluation of differences among the potential sources and background
- Quantification of contributions from the potential sources and background



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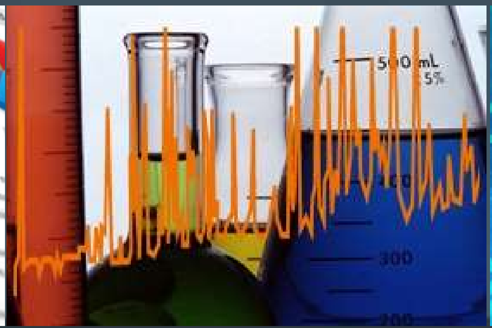
Forensic Tool Box

Source Characterization/ Causation

- Chromatograms
- Chemical fingerprints
- Biomarkers
- Diagnostic ratios
- Principal component analysis

Source Contribution

- Mixing models
- Unmixing models
- Fate and Transport models

Use of Statistical Mixing Models for PAH Apportionment has been Growing

- Powerful and versatile
- Careful application necessary
- Commentary on limitations in the literature
- This is where multiple lines of evidence (multiple models) comes into play

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DOI: 10.1080/15275922.2012.702335

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Contributed Articles

Sediment PAH Allocation Using Parent PAH Proportions and a Least Root Mean Squares Mixing Model

Kurt Herman, Eric J. Wannamaker, and Gautham B. Jegadeesan

Integrated Environmental Assessment and Management — Volume 10, Number 2—pp. 279–285
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Parsing Pyrogenic Polycyclic Aromatic Hydrocarbons: Forensic Chemistry, Receptor Models, and Source Control Policy

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Case Study

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Use of Receptor Models to Evaluate Sources of PAHs in Sediments

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Receptor models are mathematical procedures for resolving one or more of these parameters in a mixed chemical system: (1) the number of sources, (2) their chemical characteristics, and (3) the relative contribution of each source in environmental samples. These models are being used increasingly to evaluate sources of polycyclic aromatic hydrocarbons (PAHs) in sediments. As with any mathematical model, understanding the underlying assumptions is critical in interpreting the output. Three assumptions that raise particular challenges when applying receptor models to evaluate multiple sources of pyrogenic PAHs are (1) identification of all important sources, (2) stability of source profiles, and (3) linear independence of each profile. Variability within source types, and similarities among the PAH profiles of different sources, create uncertainties that must be considered when evaluating the results of receptor models. Various procedures for evaluating uncertainties have been applied in the literature, but validation and standardization of such methods are often lacking. Using a case study, this article demonstrates how a more detailed evaluation of model output can produce conclusions that differ from those initially published. While not eliminating uncertainty, we recommend a multiple-lines-of-evidence approach that includes both mixing and unmixing receptor models, along with other environmental forensic techniques.

Key Words: PAH, pavement sealer, receptor models, sediments, source control

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous constituents in urban sediments that are generally regulated as toxic and as potential carcinogens (1). Therefore, PAHs are of interest to both environmental scientists and policy makers. As a class of compounds with profiles that differ by source, they lend

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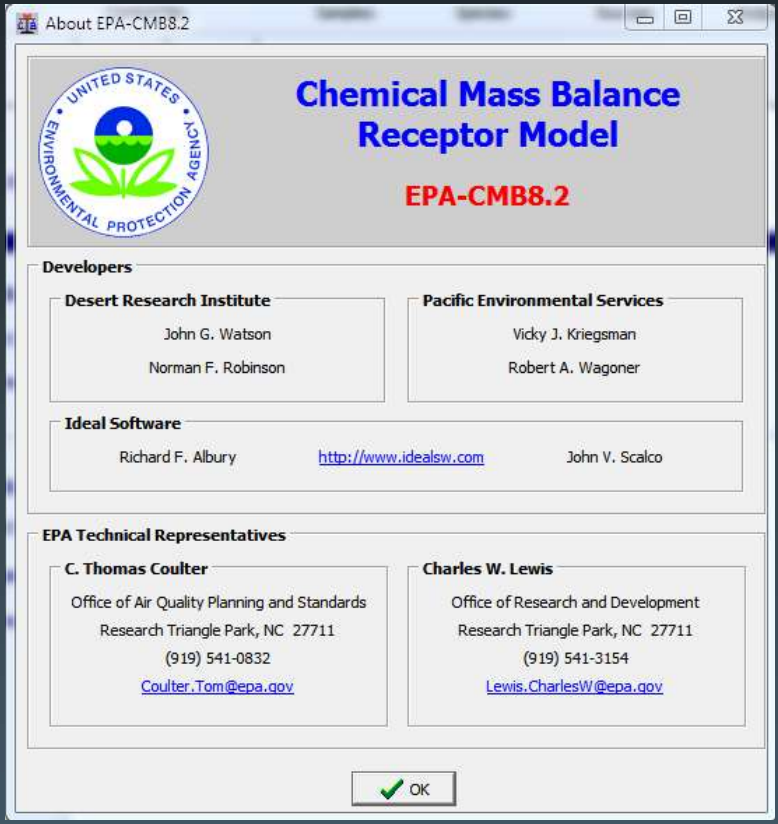
Chemical Mass Balance (CMB) Model

- Developed by US EPA
- A tool for characterizing potential sources and quantifying their contribution to the chemicals found in environmental samples
- Originally developed for air quality problems
- Increasing application sediment contamination



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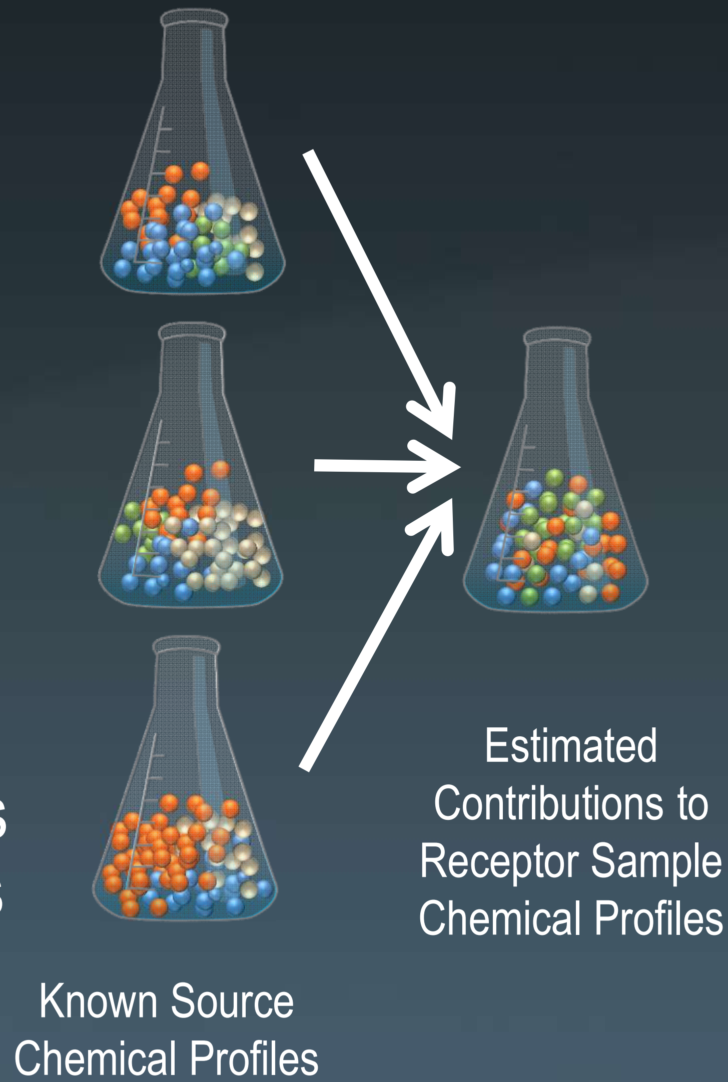
Model Inputs – Required

- Source Profiles
  - Identified potential contributing sources
  - Chemical species to be included in the calculation (i.e., PAHs)
- Receptors
  - Environmental samples that contains the same chemical species
  - Virtually no limit on the numbers of receptors
- Uncertainty
  - Uncertainties for both receptors and source profiles required
  - Standard deviation, MDL, randomly assigned constant

CMB Model Allows Sample-by-Sample Apportionment

- Model calculates best fit to a receptor (sediment) data and estimate contributions of the sources
- Application to sediments
  - Individual sample results
  - Can be combined for overall evaluation
- The validity of the results depends on the validity of the source inputs



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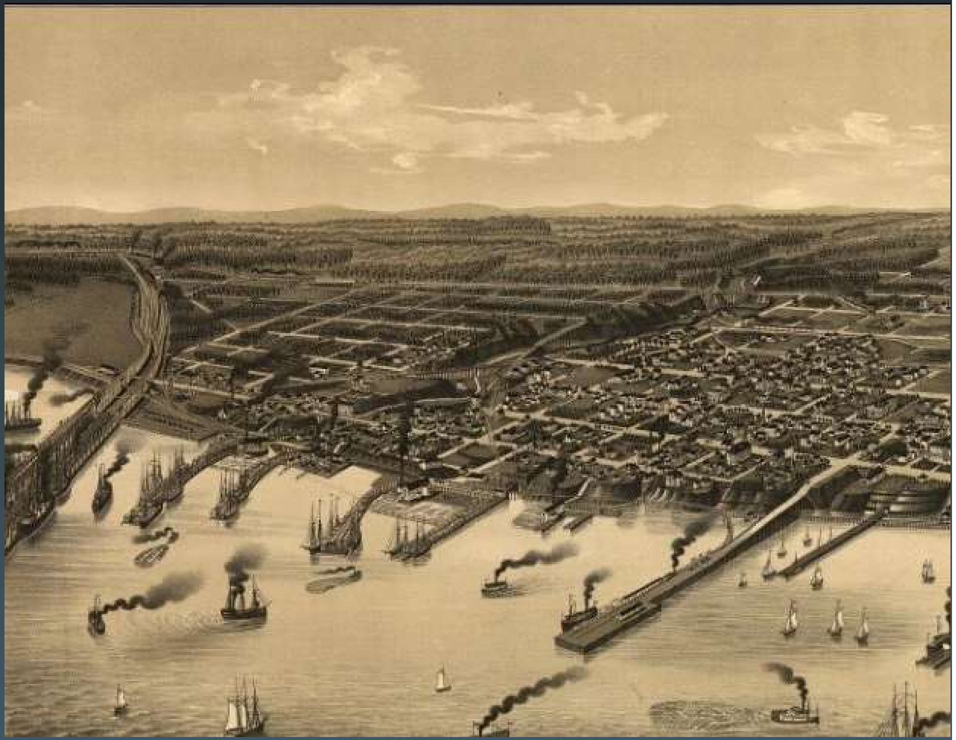
CASE STUDY I

- Literature-based sources
v. Field collected sample-based sources

PAH Source Attribution at a Complex Great Lakes National Priorities List (NPL) Site

- Historical industrial and other activities contributed PAHs to the NPL Site including adjacent sediments
- Two chemically distinct sources:
  - Source 1 (wood treatment facility)
  - Source 2 (former MGP)



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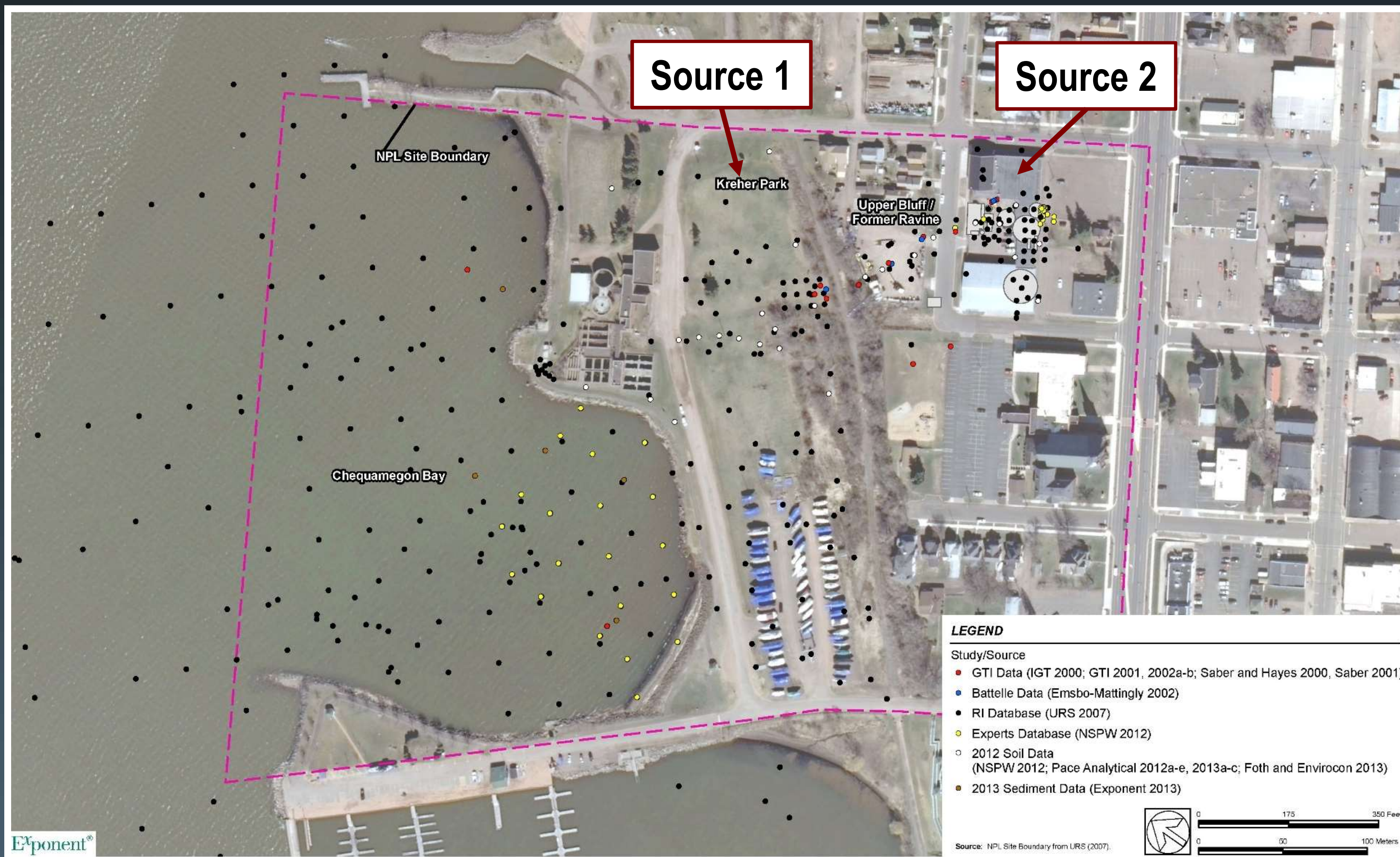
Extensive Data Available for the Site – Limited Forensic Data



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Identifying Appropriate Source Profiles Is a Critical Step

- Literature-based source profiles
  - Peer reviewed journals
  - Government reports
- Site samples best represented the materials that were originally released to sediments
  - Soils
  - NAPLs

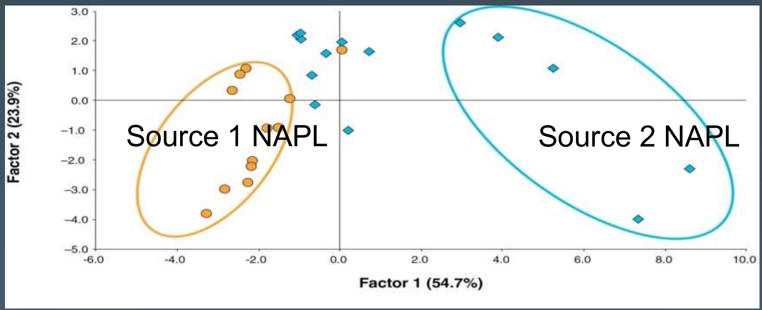
CMB Setup

Literature-based

- Literature survey
- Representative PAH profiles were obtanied
  - Creosote (n=7)
  - MGP (n=4)
- 9 PAHs as chemical species
- 193 sediment samples as receptors

Field collected sample-based

- Collected soil and NAPL samples
- PCA for source sample selection
- Averages of contributing site samples
- 9 PAHs as chemical species
- 193 sediment samples as receptors



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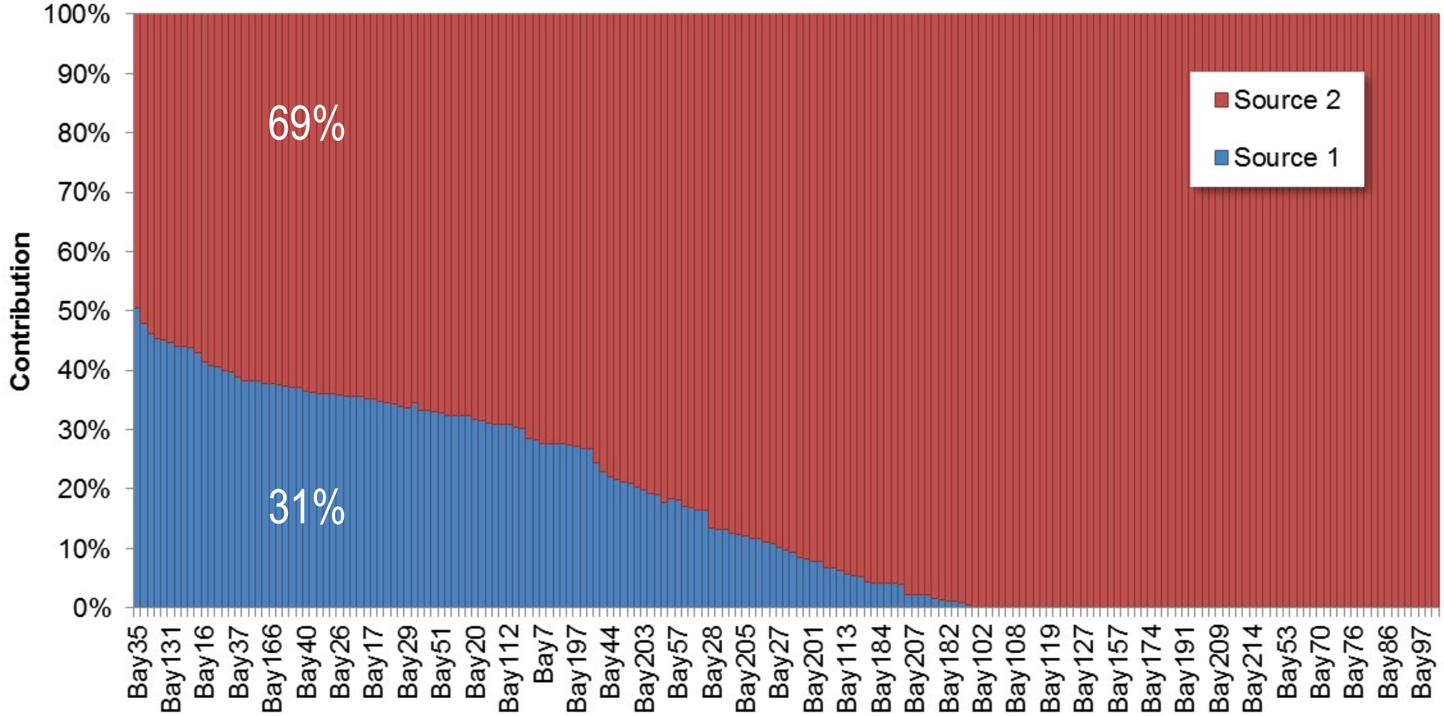
CMB Results Using Literature-based Source Profiles



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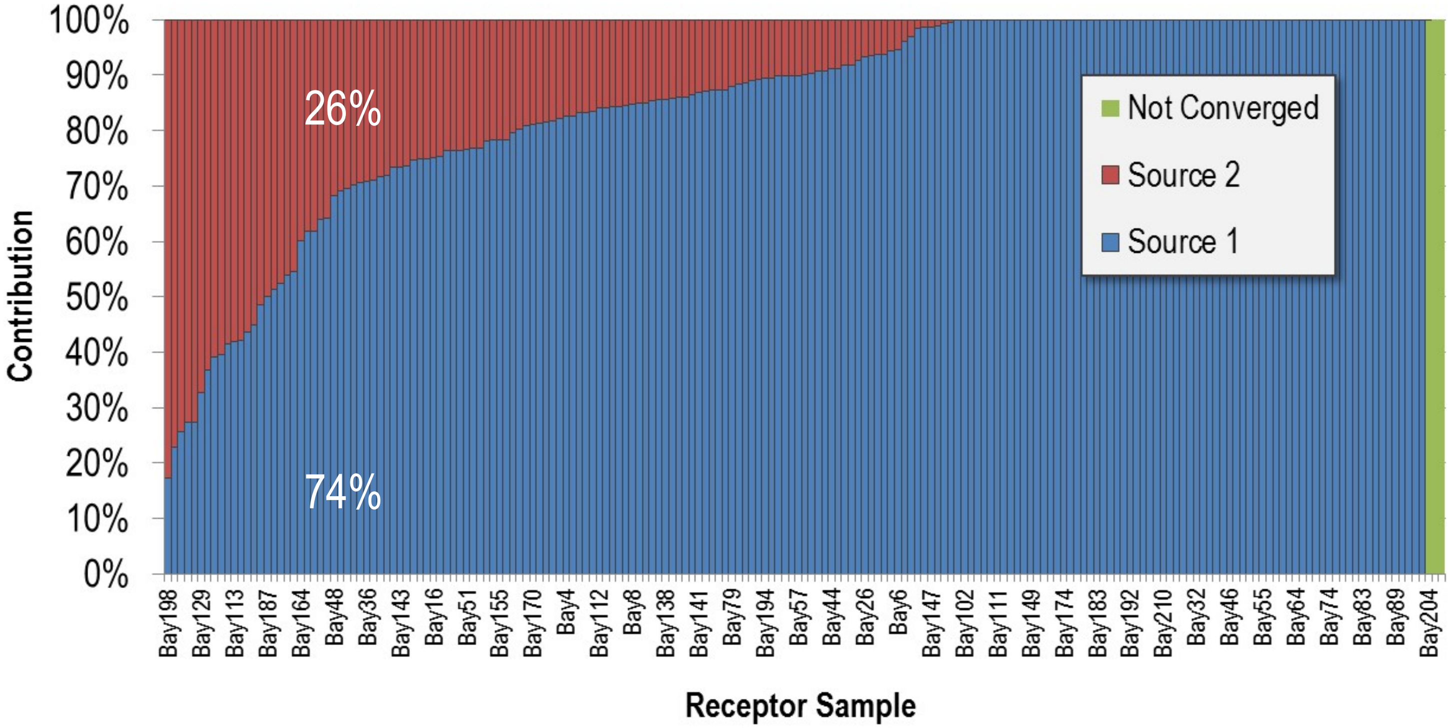
CMB Results Using Field Collected Sample-based Source Profiles (Soil samples)



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Additional Field sample-based CMB Results

Analysis	Source 1 (%)	Source 2 (%)	Reference/ Background (%)	Not Allocated/ Inconclusive (%)
PAH Proportion Mixing Model 1	92	8	--	--
PAH Proportion Mixing Model 2	90	10	--	--
PAH Proportion Mixing Model 3	87	13	--	--
Soil Double Ratio Apportionment	85	6	--	8
CMB Run 1 (2 soil sources)	74	26	--	--
CMB Run 2a (2 NAPL sources)	93	7	--	--
CMB Run 2b (same as 2a + additional data)	91	9	--	--
CMB Run 3 (2 NAPL + background sources)	91	7	2	--
CMB Run 4 (4 NAPL sources)	97	3	--	--

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Different Allocation Models Pointed to the Same Direction

Analysis	Source 1 (%)	Source 2 (%)	Reference/ Background (%)	Not Allocated/ Inconclusive (%)
PAH Proportion Mixing Model 1	92	8	--	--
PAH Proportion Mixing Model 2	90	10	--	--
PAH Proportion Mixing Model 3	87	13	--	--
Soil Double Ratio Apportionment	85	6	--	8
CMB Run 1 (2 soil sources)	74	26	--	--
CMB Run 2a (2 NAPL sources)	93	7	--	--
CMB Run 2b (same as 2a + additional data)	91	9	--	--
CMB Run 3 (2 NAPL + background sources)	91	7	2	--
CMB Run 4 (4 NAPL sources)	97	3	--	--

CASE STUDY II

- Refined Tar Pavement Sealers (RTS) in Urban Lake Sediments

The Role of Refined Tar Pavement Sealers (RTS) in Urban Lake Sediments

- Van Metre and Mahler (2010) used CMB to evaluate whether RTS is an important contributor to PAH urban background
- Source inputs, calculated from various types of published data, have not been validated to be appropriate
- Authors highlight results of just 4 out of over 200 model runs
- Others are applying the same approach to similar sediment data sets

Proper Selection is Critical: Minor Changes in Inputs Can Result in Significantly Different Outputs

Table 1
PAH source categories and source profiles considered. [CT, coal-tar-based].

Source category	PAH source	Reference
Coal combustion	Power plant emissions	Li et al., 2003
	Residential heating emissions	Li et al., 2003
	Coke oven emissions	Li et al., 2003
	Coal average (defined in Li et al., 2003)	Li et al., 2003
Vehicle related	Diesel vehicle particulate emissions	Li et al., 2003
	Gasoline vehicle particulate emissions	Li et al., 2003
	Traffic tunnel air	Li et al., 2003
	Traffic average (defined in Li et al., 2003)	Li et al., 2003
	Used motor oil 1	Wang et al., 2000
	Used motor oil 2	Boonyatumanond et al., 2007
	Tire particles	Boonyatumanond et al., 2007
	Asphalt	Boonyatumanond et al., 2007
	NIST diesel particles	NIST, 2000
Fuel-oil combustion	Fuel-oil combustion particles	Li et al., 1999
Wood burning	Pine-wood soot particles	Schauer et al., 2001
CT-sealcoat related	NIST coal tar	NIST, 1992
	CT-sealcoat products	Mahler et al., 2005
	CT-sealcoat scrapings, fresh	Mahler et al., 2005
	CT-sealcoat scrapings, Milwaukee	Van Metre et al., 2008
	CT-sealcoat scrapings, Austin	Mahler et al., 2004
	CT-sealcoated pavement dust, six cities (SC-dust)	Mahler et al., 2004; Van Metre et al., 2008
	CT-sealcoated pavement dust, Austin (SC-Austin)	Mahler et al., 2004; Van Metre et al., 2008

- Sediment from 40 lakes in urban areas across the US
- Sources – mix of literature-based source profiles and field-collected samples-based source profiles
- Lost site specific characteristics

Proper Selection is Critical: Minor Changes in Inputs Can Result in Significantly Different Outputs

Paper only included the results of 4 out of over 200 model runs conducted

			CMB Modeled Contribution (%)			
RTS or Urban Dust Source Profile	**Model vs Measured Correlation [r]**	**Parking Lot Dust**	**Vehicle Tunnel**	**Wood Smoke**	**Coal**	**Fuel oil**
RTS Sealed Parking Lot Dust	0.99	**46**	36	5.0	9.0	3.0

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Proper Selection is Critical: Minor Changes in Inputs Can Result in Significantly Different Outputs

Average CMB modeled source contributions for 4 runs with different source profiles

			CMB Modeled Contribution (%)			
RTS or Urban Dust Source Profile	**Model vs Measured Correlation [r]**	**RTS or Dust Source**	**Vehicle Tunnel**	**Wood Smoke**	**Coal**	**Fuel oil**
RTS Sealed Lot Dust	0.99	**46**	36	5.0	9.0	3.0
Unsealed Lot Dust	0.97	**60**	25	11	3.5	0.4
RTS Test Plot	0.98	**0.0**	42	57	1.0	0.0
No RTS	0.98	--	48	51	1.2	0.0

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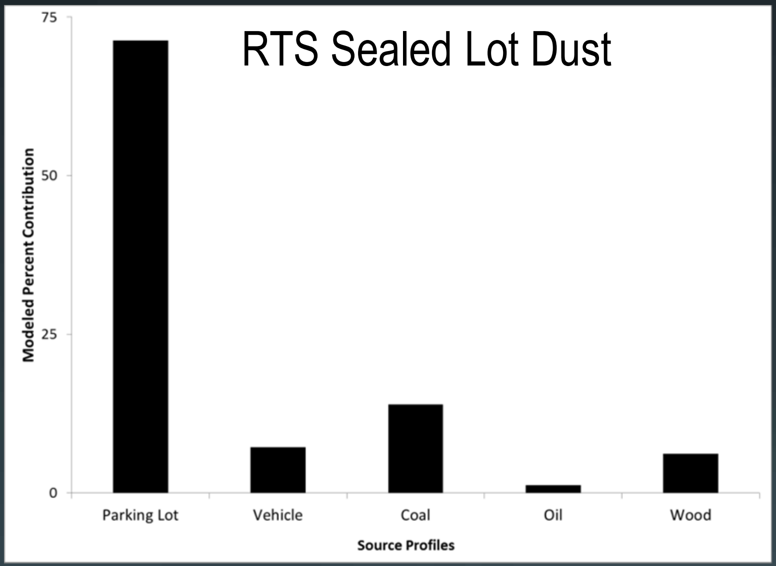
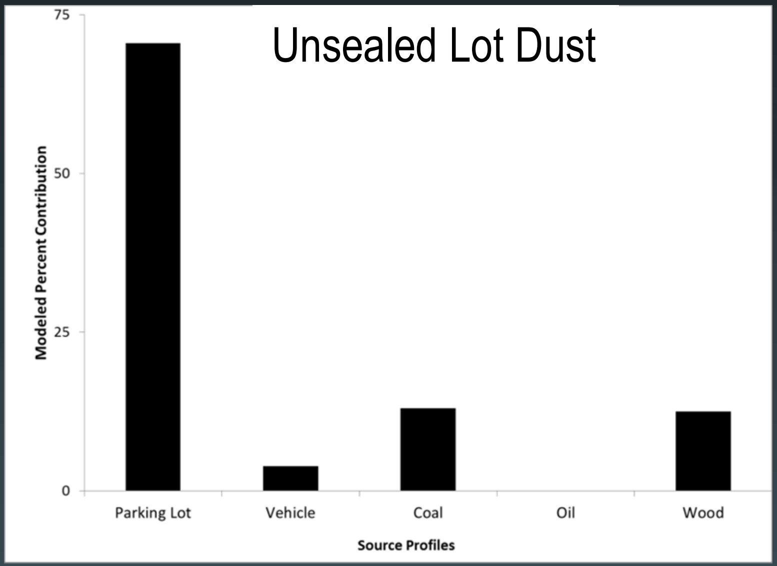
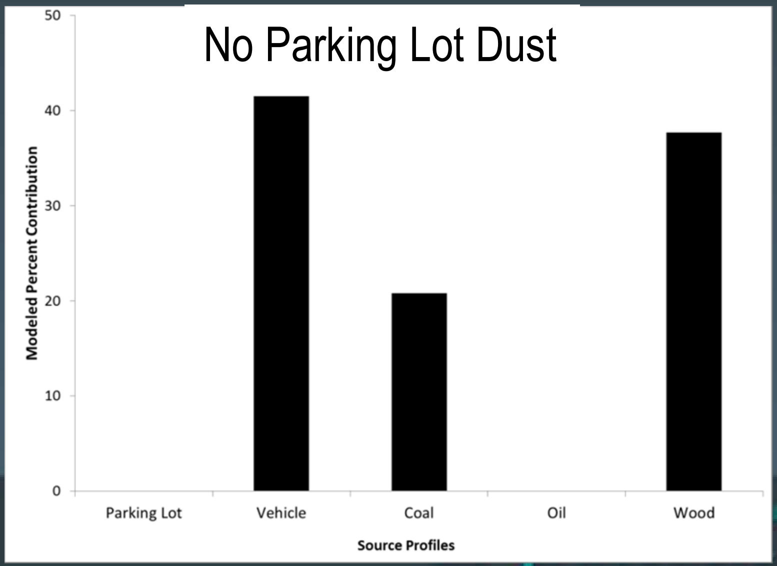
It is Critical to Run Proper Controls

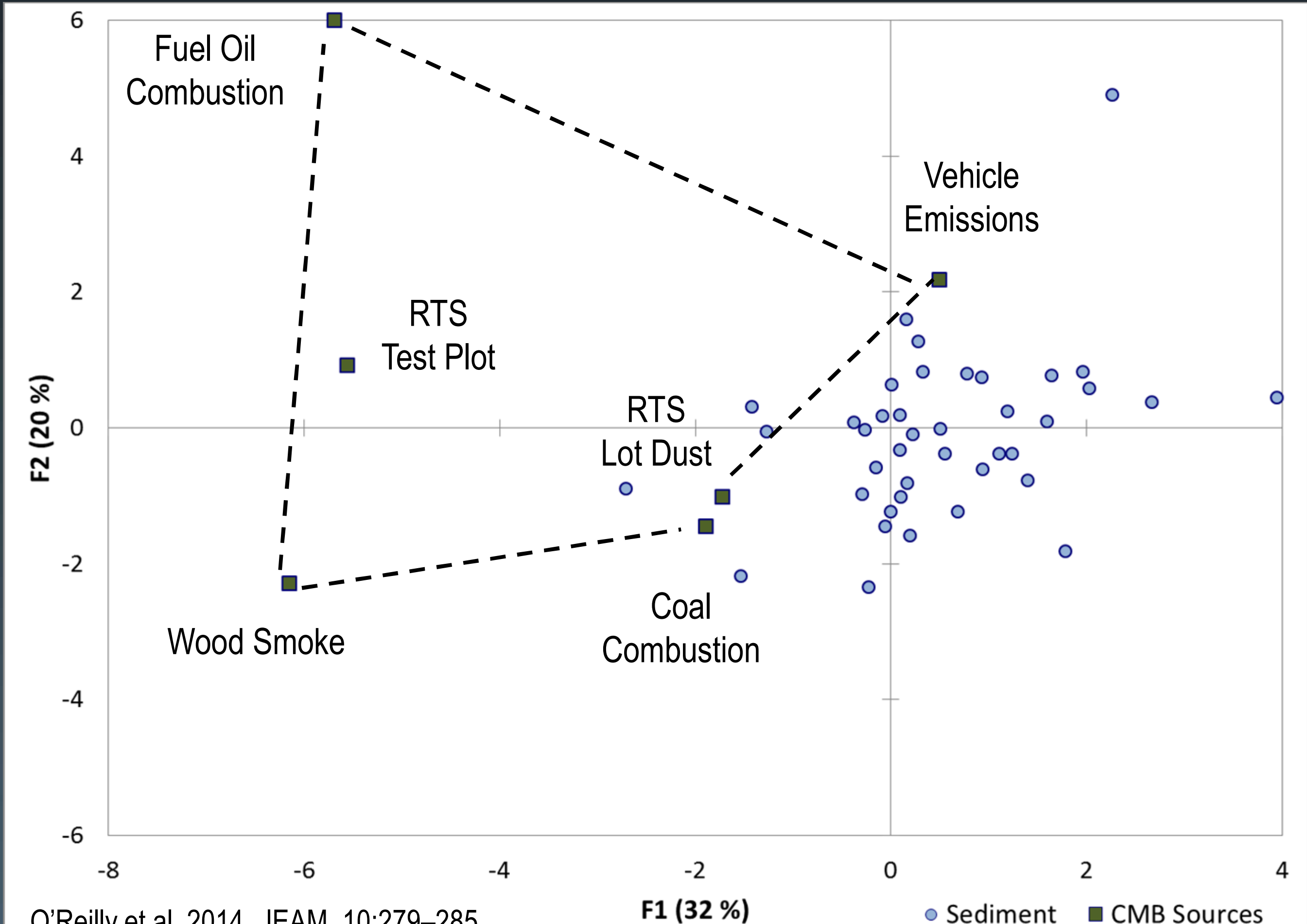




- The calculated contribution of sealed and unsealed parking lots was the essentially the same
- Sediment chemistry could be modeled in the absence of any parking lot contribution



Use of PCA to Identify Appropriate CMB Source Profiles



O'Reilly et al. 2014. IEAM, 10:279–285

Summary

- CMB is simple, powerful, and versatile.
- CMB, however, has apparent limitations.
  - Results can be totally different under different conditions.
  - Uncertainties, outliers, ND
- Proper source selection is critical.
- The validity of the results depends on the validity of the source inputs.
- Negative control can be a good option to consider.
- "multiple lines of evidence" approach is recommended.